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Thermal Degradation Behavior of Siloxane Elastomer Impregnated Carbon Nanotube Aerogel Networks

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Thermal Degradation Behavior of Siloxane Elastomer Impregnated Carbon Nanotube Areogel Networks



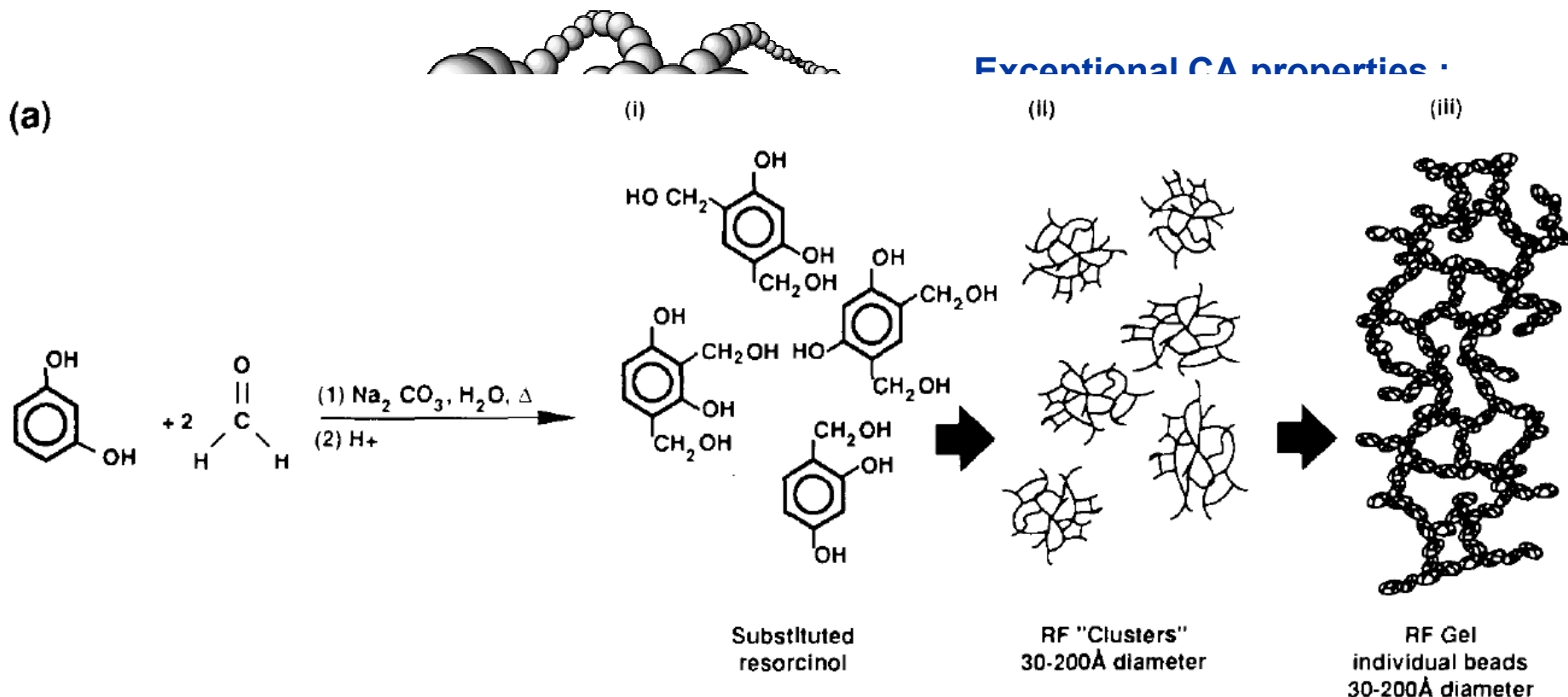
James P. Lewicki, Brian P. Mayer, & Marcus
A. Worsley

PacificChem, Hawaii Dec. 2010

LLNL-CONF-464983

Novel Nanocarbons: Carbon Aerogels

- CAs are unique porous materials comprised of 3D networks of interconnected nanometer-sized carbon particles



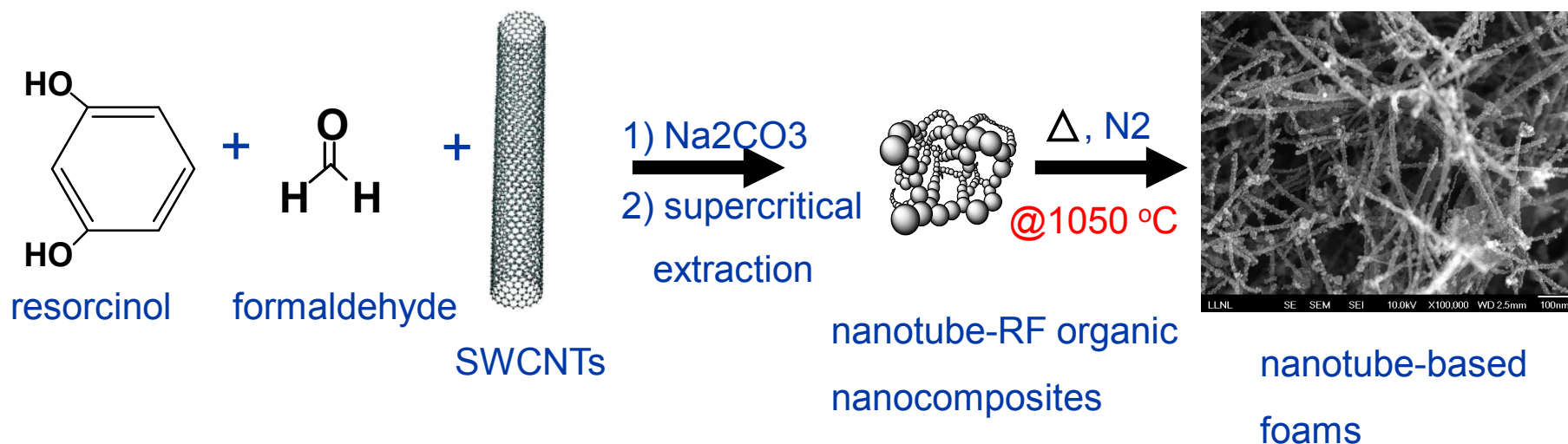
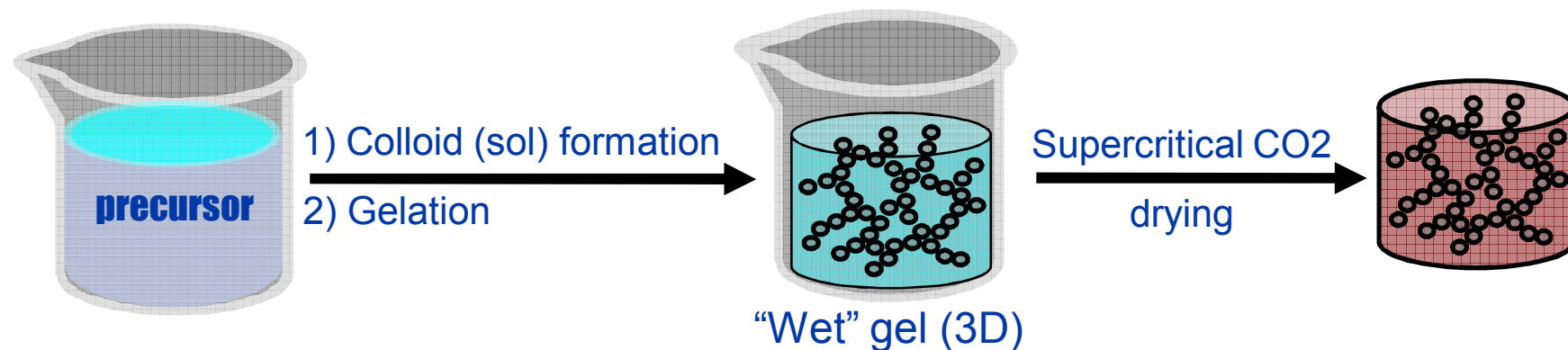
Flexibility of sol-gel synthesis:

- Allows addition of CNTs to sol-gel reaction to create CNT-CA*

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Synthesis of CNT Areogel Foams

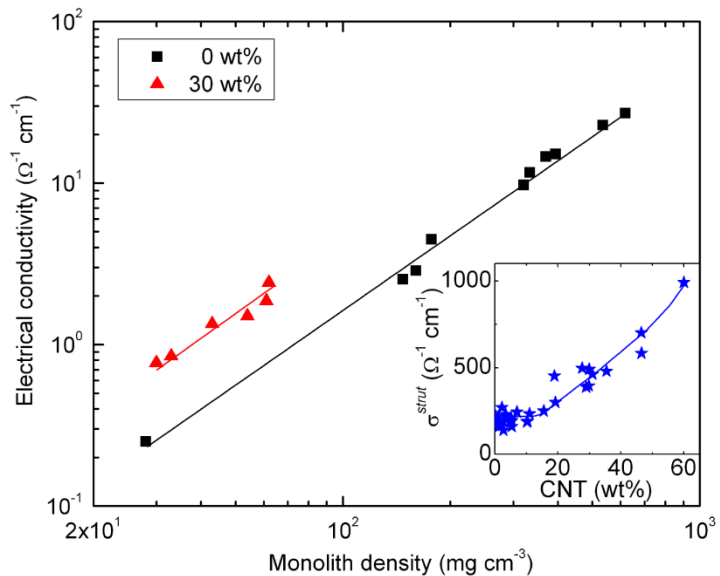
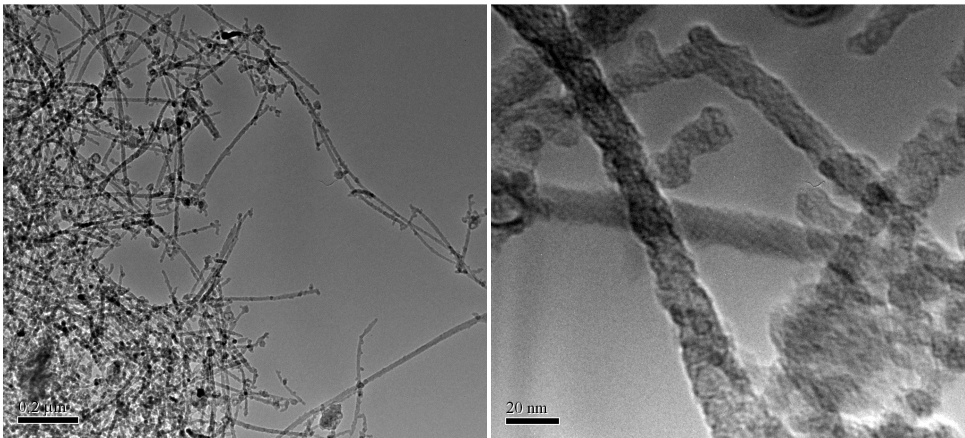


We have made ultralow-density graphitic carbon nanofoams with unprecedented properties



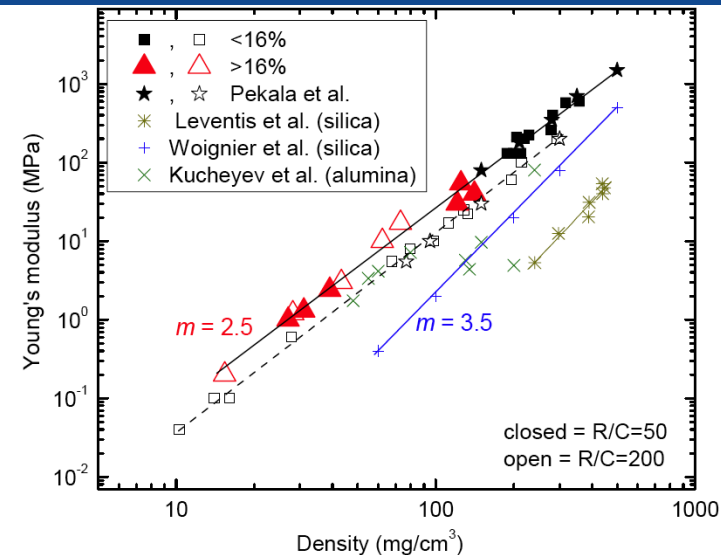
Physical properties of CNT-based aerogel (CNT-CA) foams

Randomly interconnected nanotube bundles are “glued” together by graphitic carbon aerogel particles.



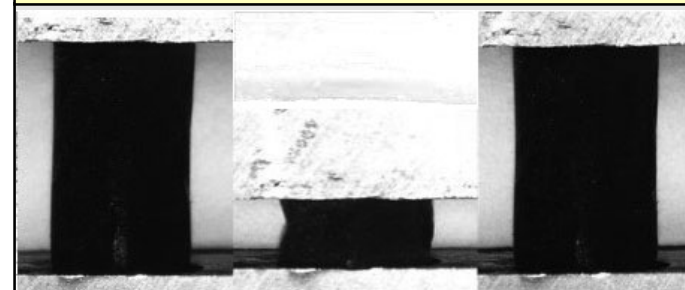
Electrically conductive at low density

These high-surface area (~200 m²/g), conductive CNT-CA serve as an extremely low-density scaffold for a MOx/C, polymers etc.



Stiffest low-density solid reported

Large elastic range



Complete recovery after uniaxial compression to ~70% strain

Worsley *et al*, *Appl. Phys. Lett.* **94**, 073115 (2009).

Worsley *et al*, *J. Mater. Chem.* **19**, 3370 (2009).

Option:Additional Information

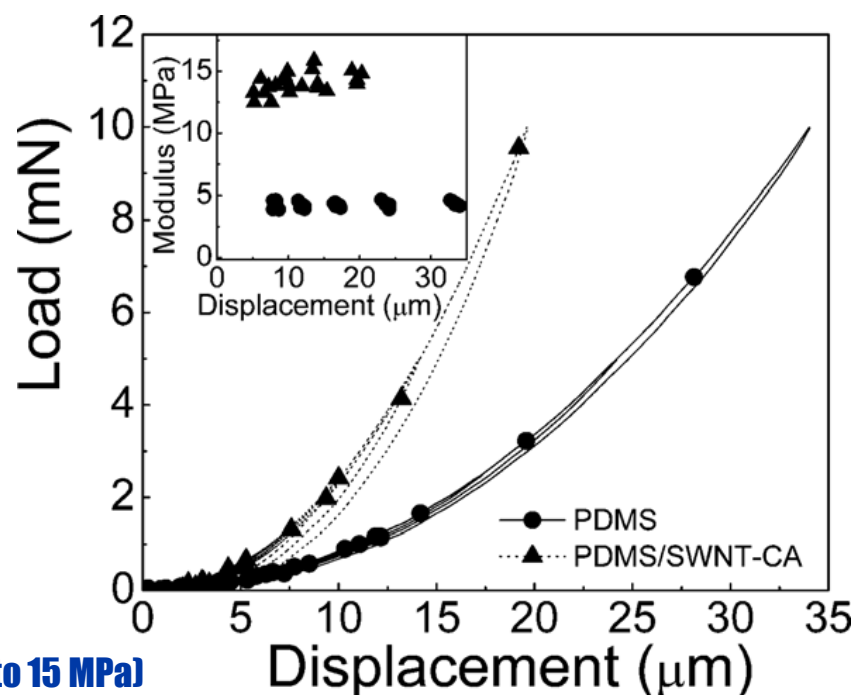
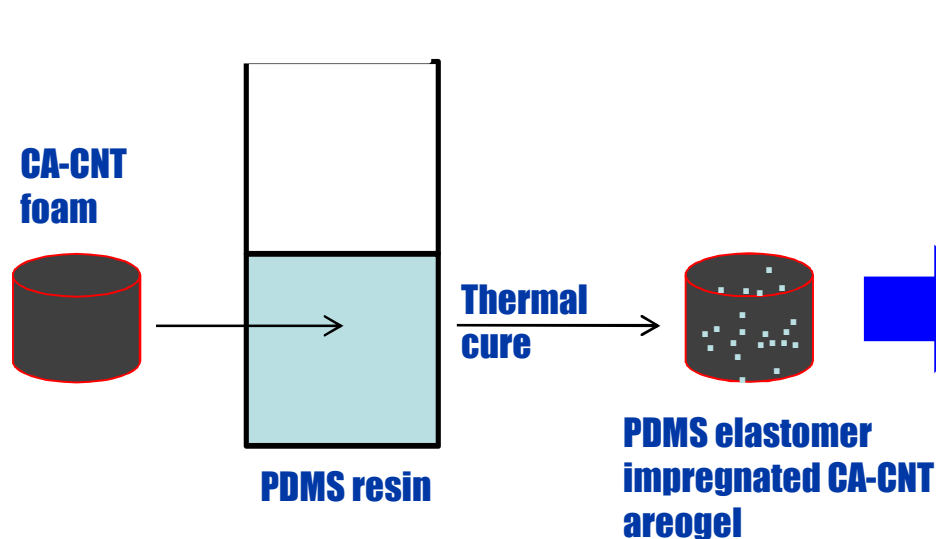
Applications of CNT-Carbon Areogel foams

INCORPORATION INTO A POLYMER MATRIX



CNT-CA foam-PDMS composite materials

- It is possible to combine these novel, ultra-low density areogel networks with siloxane polymer systems to form areogel-siloxane composites with novel physical properties:



PDMS/CA-CNT composites:

- Greatly increased mechanical properties (γ -Mod increase from 5 to 15 MPa)**
- Highly electrically conductive: 1 S cm^{-1} vs. $<0.001 \text{ S cm}^{-1}$**

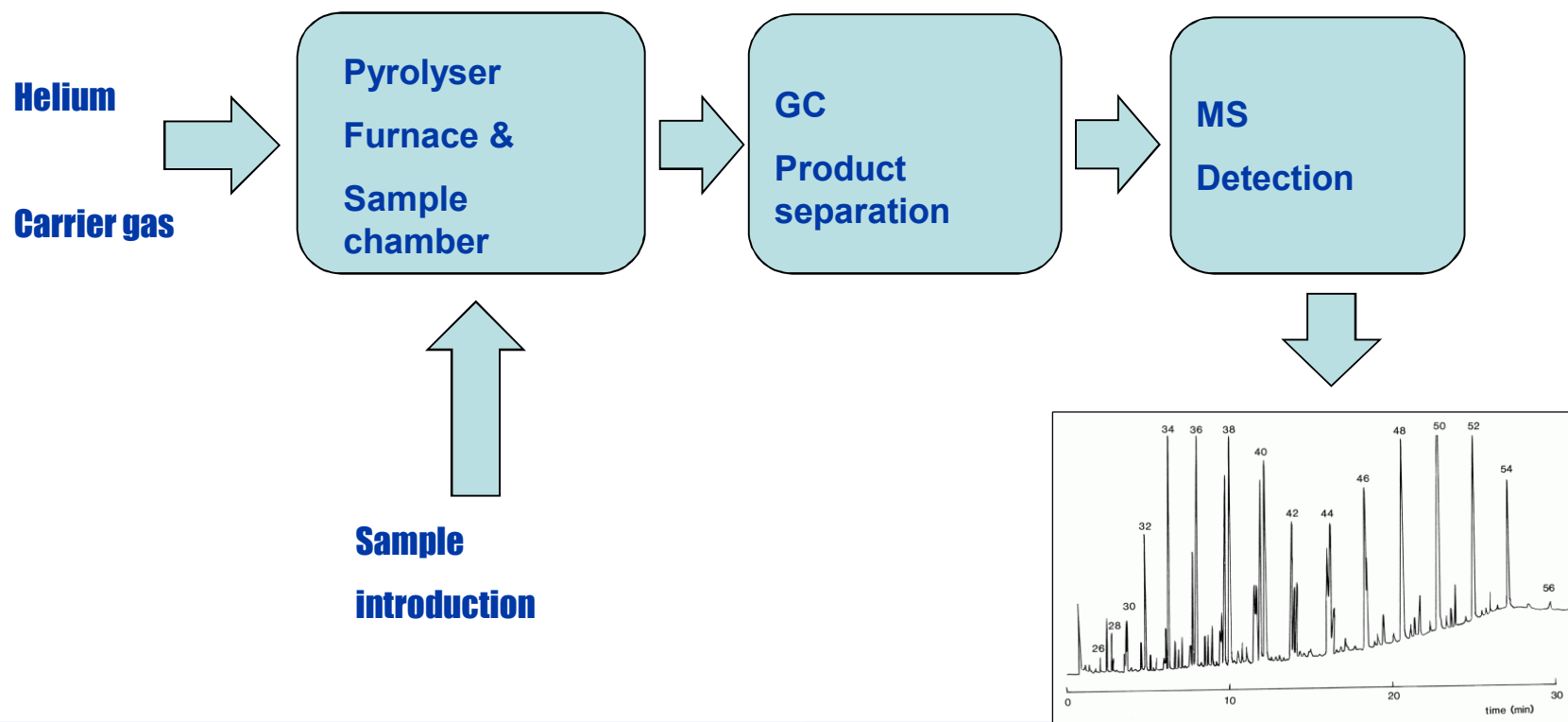
Thermal degradation behavior of PDMS-CNT-CA composites

WHAT EFFECT DOES THE SCAFFOLD HAVE ON THE MATRIX STABILITY?



Pyrolysis GC-MS – the technique

- The basic experimental set-up consists of a 'pyrolysis head' connected online to a standard gas chromatography mass spectrometry system



Utility and advantages of the technique

- Small sample size (1-2 mg)
- Wide dynamic range of heating rates and temperatures (0.1-999 deg. C/min and max temperature of 1200-1400 deg. C.)
- Small sample size and wide dynamic range allow the investigation of many volatiles evolution processes, from low temperature offgassing to non-diffusion limited high temperature thermal degradation.
- GC-MS for volatile product separation and detection: high sensitivity for the detection of trace products and broad mass range of detection from small molecules to larger species.



Py-GC-MS capability at LLNL

- CDS analytical 5150 pyroprobe system coupled to Agilent 7980 series GC-MS system.



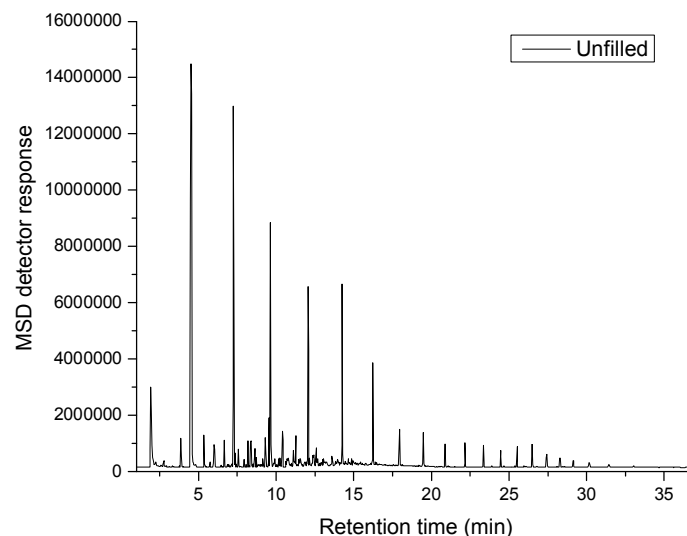
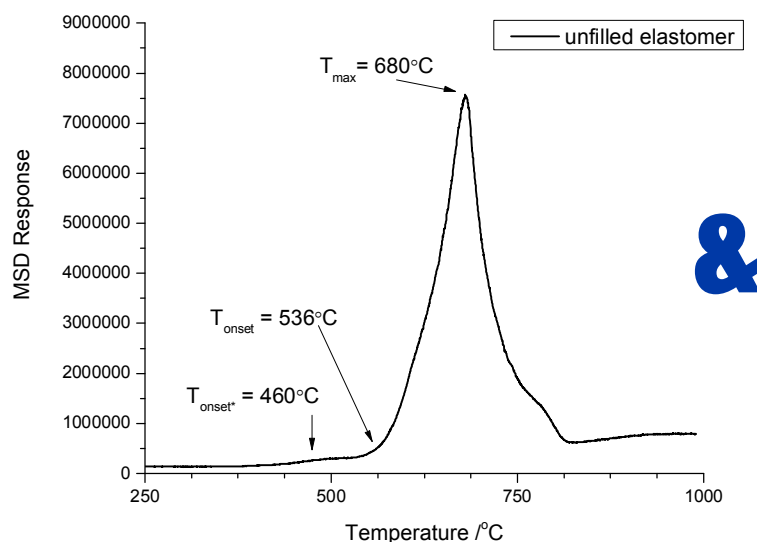
Platinum filament pyrolyzer for pulse pyrolysis and multistep, programmed pyrolysis

Filament Temperature:
Programmable in 1°C increments to 1400°C

Heating Rates: 0.01 to 20.0°C/ms (10 to 20,000°C/second)

Probing the thermal stability of the composites with Py-GC-MS

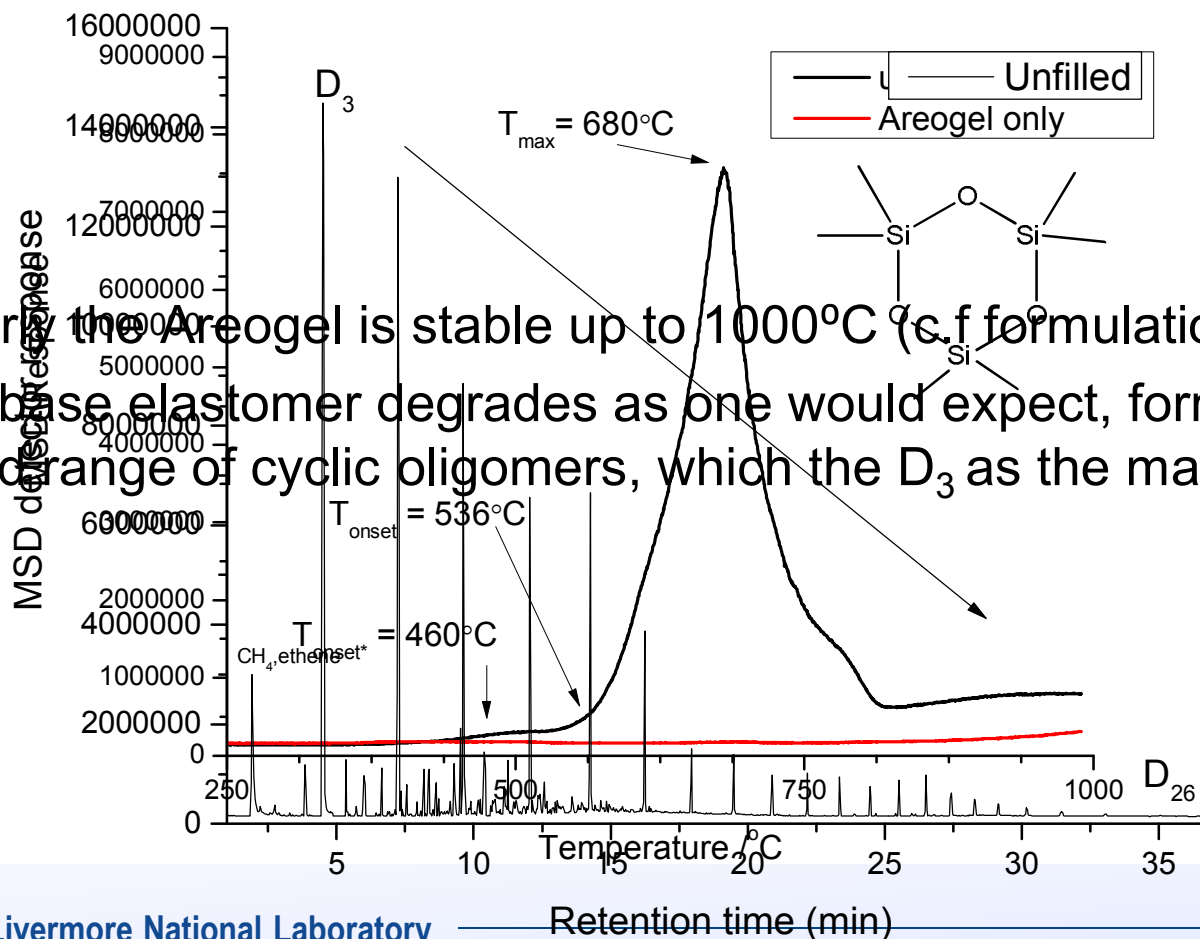
- Pyrolysis GC-MS had been utilized to characterize the thermal stability and degradation chemistry of the siloxane-CA-CNT composites



- Master curves yield information on the overall stability/degradation process and GC-MS product separation yields chemical information

Degradation of the base components

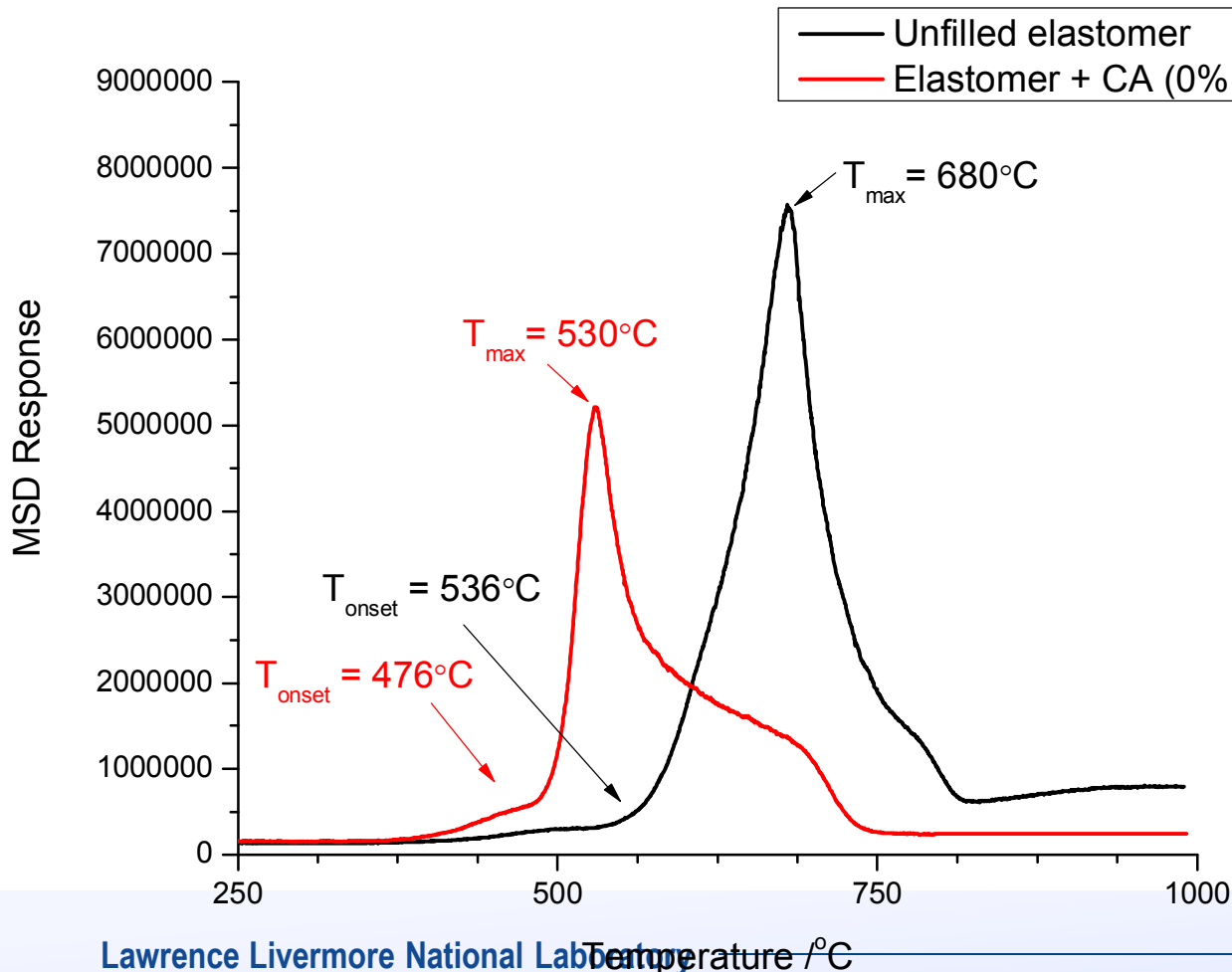
- The degradation profile of the PDMS elastomer base was compared to that of the base carbon areogel component



- Clearly the Areogel is stable up to 1000°C (c.f formulation)
- The base elastomer degrades as one would expect, forming a broad range of cyclic oligomers, which the D_3 as the main product

The influence of the carbon areogel

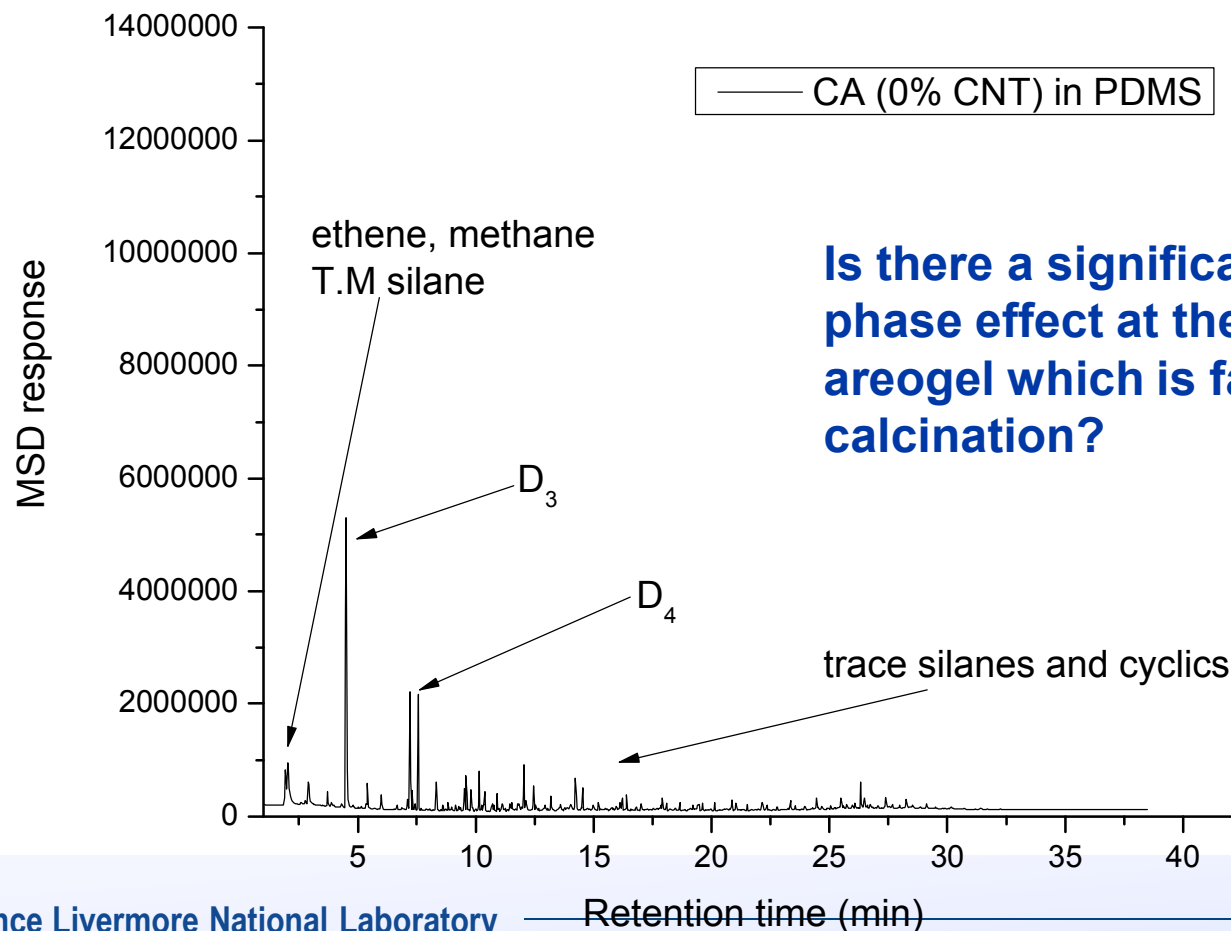
- The carbon areogel alone has a rather profound effect on the stability of the siloxane matrix:



- 60°C decrease in onset degradation temperature
- 150 °C decrease in onset degradation temperature
- Indications of the introduction of a high temperature tail

The influence of the carbon areogel

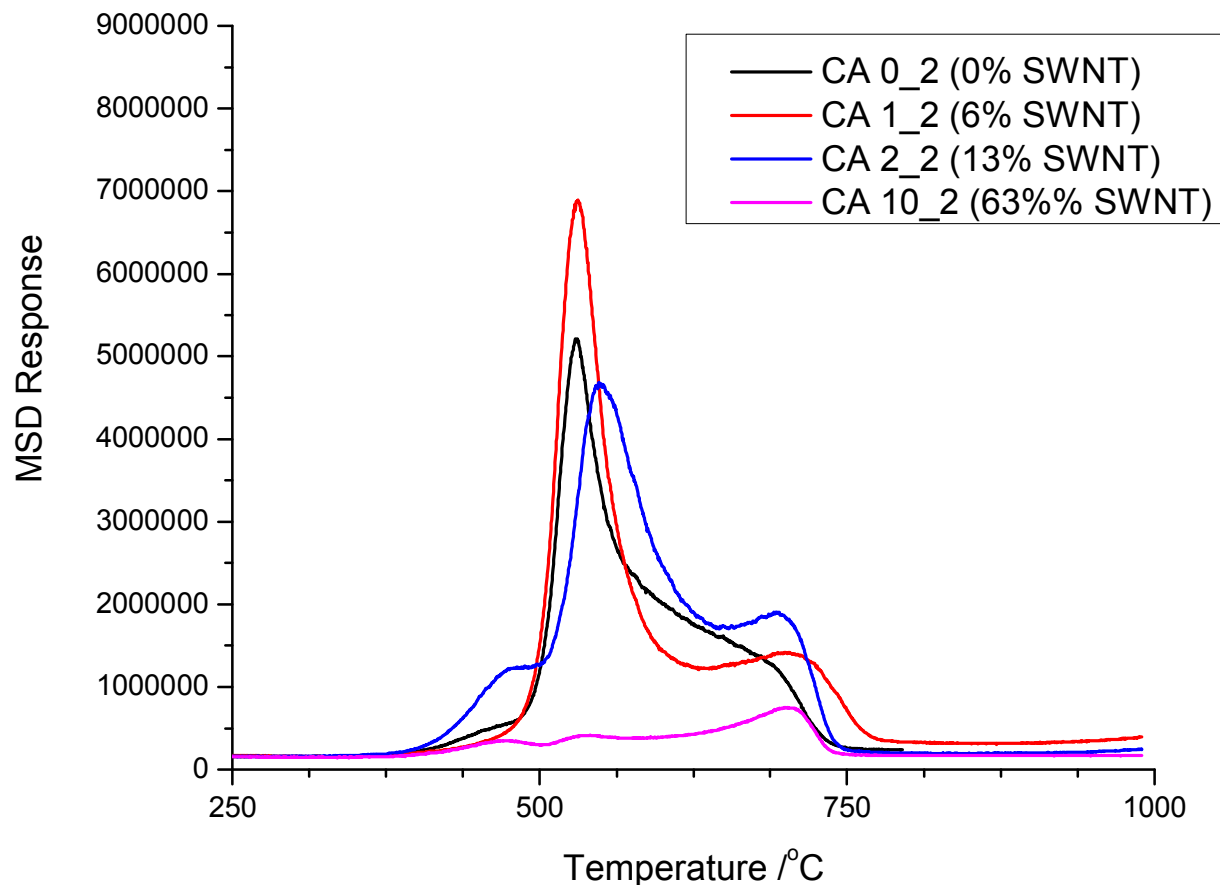
- Interestingly, the normally resistant to change PDMS degradation chemistry is significantly altered in the presence of the CA areogel:



Is there a significant condensed phase effect at the surface of the areogel which is favoring calcination?



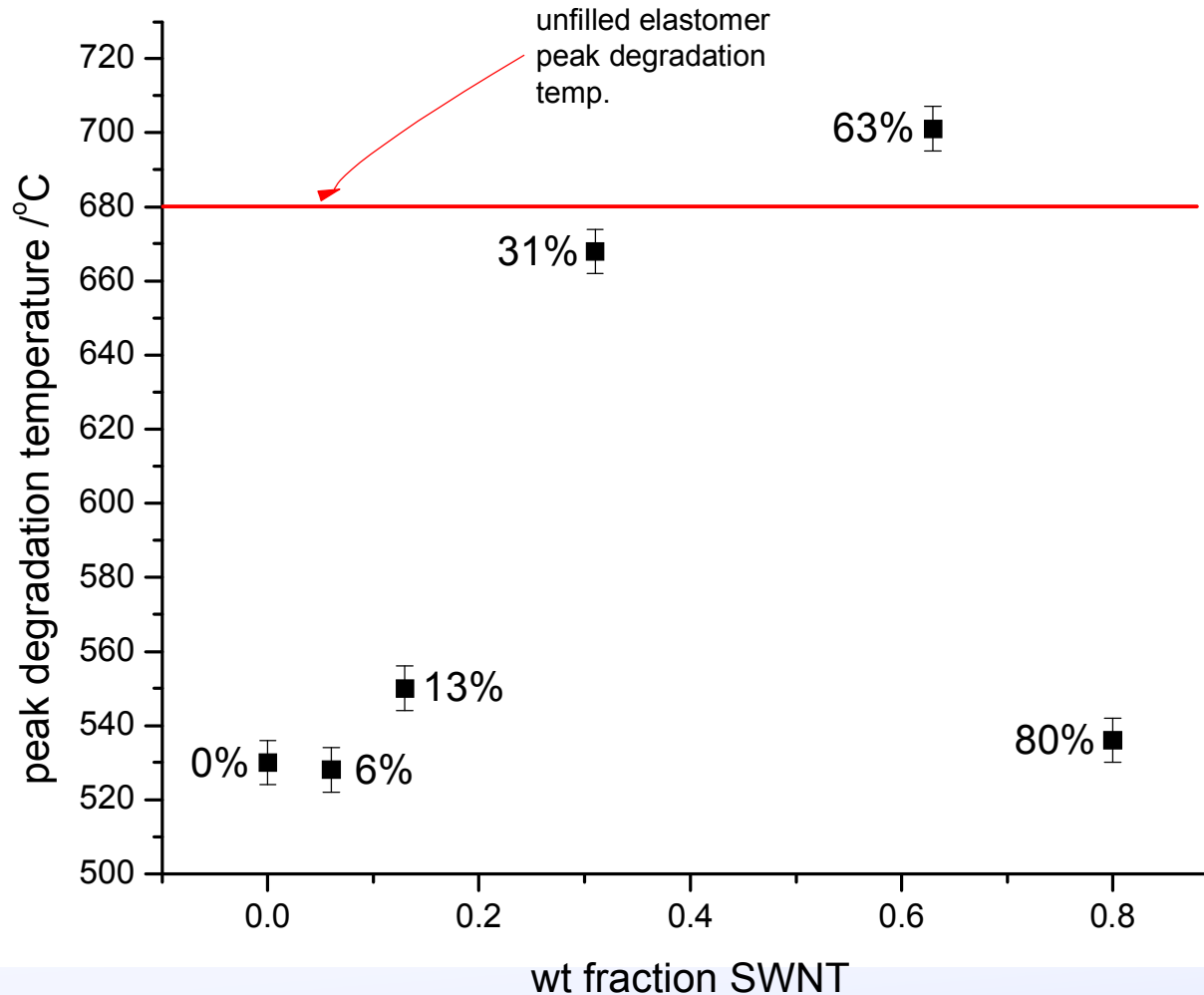
How do the nanotube reinforced systems effect the chemistry?



- If we compare a series of the composites it becomes clear that the inclusion of CNT's into the system, further perturb the degradation profile.
- At high CNT loadings the overall level of volatile degradation products decrease to extremely low levels



How do the nanotube reinforced systems effect the chemistry?



Can we determine why this network affects the degradation chemistry so profoundly?

MQ NMR ANALYSIS OF THE PDMS-CNT-CA COMPOSITES



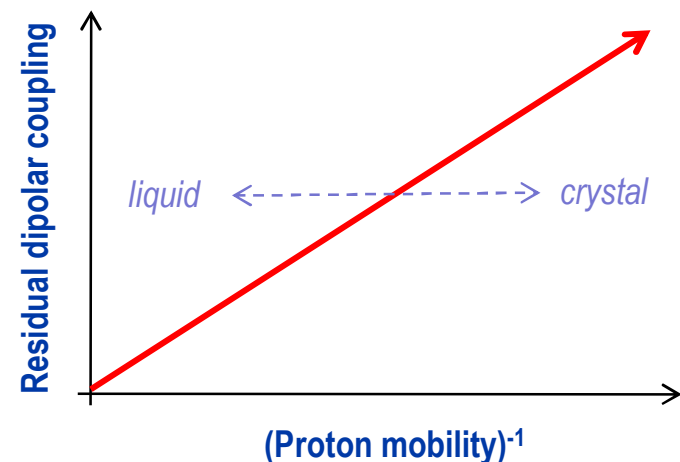
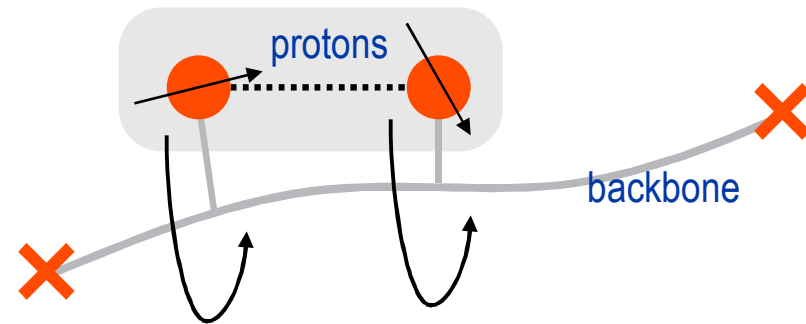
ssNMR as a complimentary technique to assess mobility in polymeric systems

- Double Quantum NMR an efficient way to probe chain mobility
 - Via proton-proton dipolar interaction
 - Local interaction depends directly on ability of chain to reorient
 - Highly dependent on topological constraints:
 - Chemical crosslinks, physical interactions, chain entanglement, etc.
 - Parameterized by a **residual dipolar coupling**, D_{res} , measuring interaction strength between two protons along the chain length

The more restricted proton mobility becomes

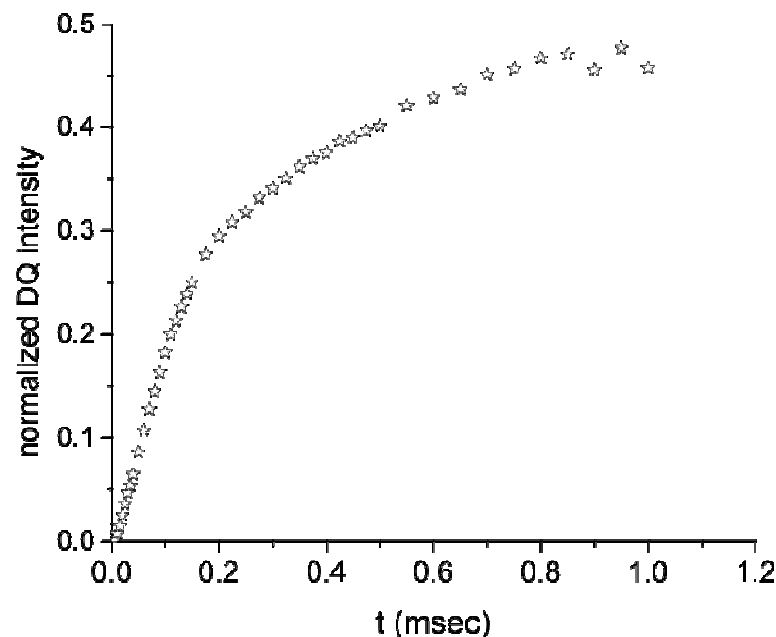
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The larger the value of D_{res} .



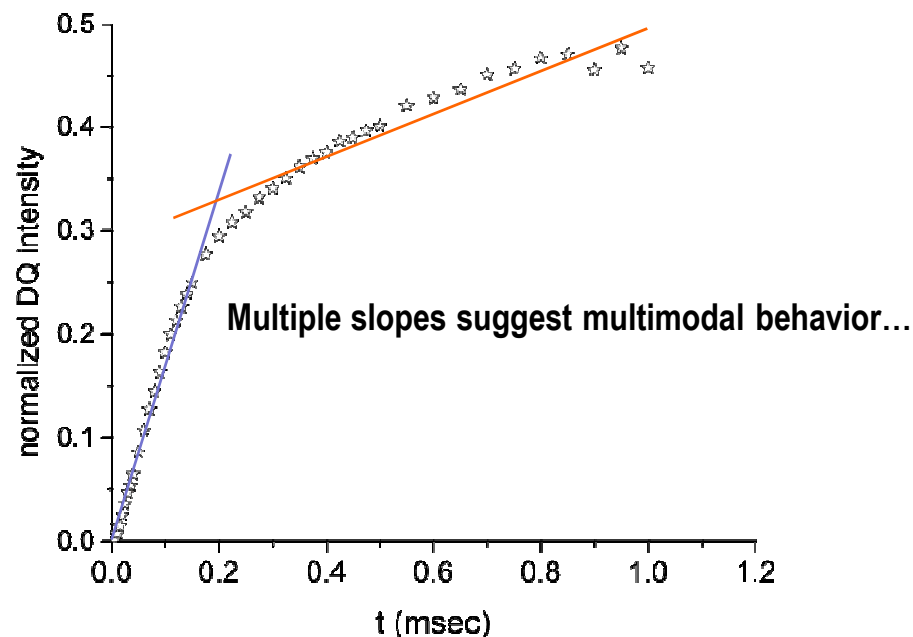
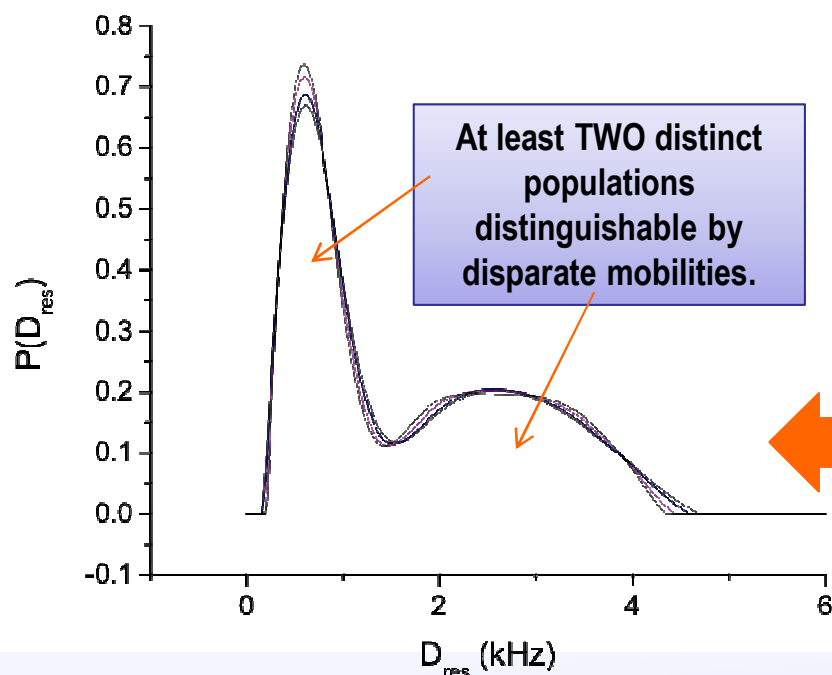
Distributions of ssNMR-derived D_{res} reveal both morphological and dynamical details

- Can extract distributions of residual dipolar couplings from DQ coherence build-up as measured by ^1H NMR.



Distributions of ssNMR-derived D_{res} reveal both morphological and dynamical details

- Can extract distributions of residual dipolar couplings from DQ coherence build-up as measured by ^1H NMR.
- For multicomponent build-ups, can extract distributions in a *model-free* way.
 - FTIKREG (regularization software)



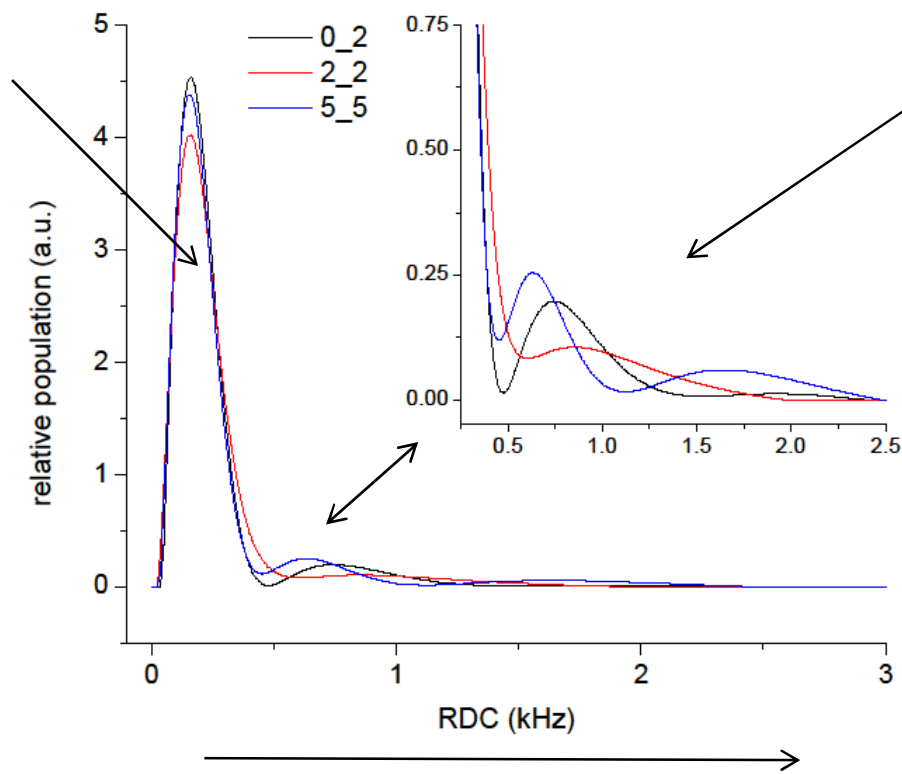
FTIKREG software

What can DQ NMR Tell us about these materials

- Show below are the extracted RDC distributions obtained from the CA-CNT-siloxane composites

As expected, the majority of the PDMS chains are generally unperturbed by the presence of the areogel scaffold and behave like the base monomodal network (not shown)

This is attributed to the low density and of the carbon scaffold



Significantly, however we observe a distinct secondary population with decreased mobility

Evidence of chains that are partially immobilized/associated with the carbon/CNT scaffold.

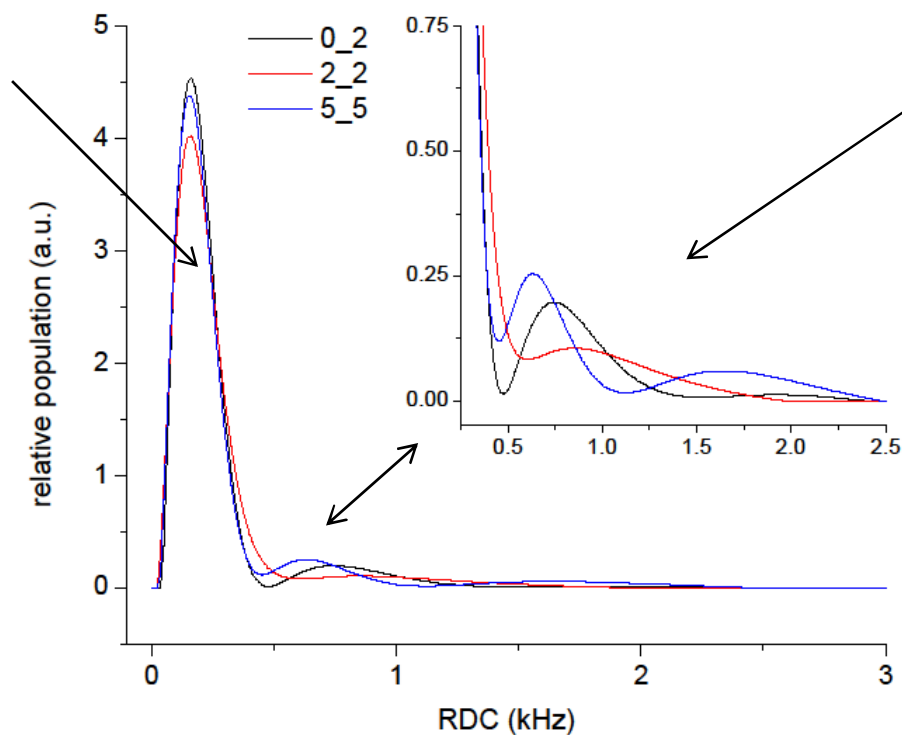
The network is stiffened around the scaffold.

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Decreasing chain mobility →

What do we know?

- Physical entrapment
- Diffusion control
- ‘matrix propping’



What don't we know?



What may be happening?

- PCA.
- More deg.
- More NMR



Theodore Baumann, Sarah C. Chinn & Robert S. Maxwell

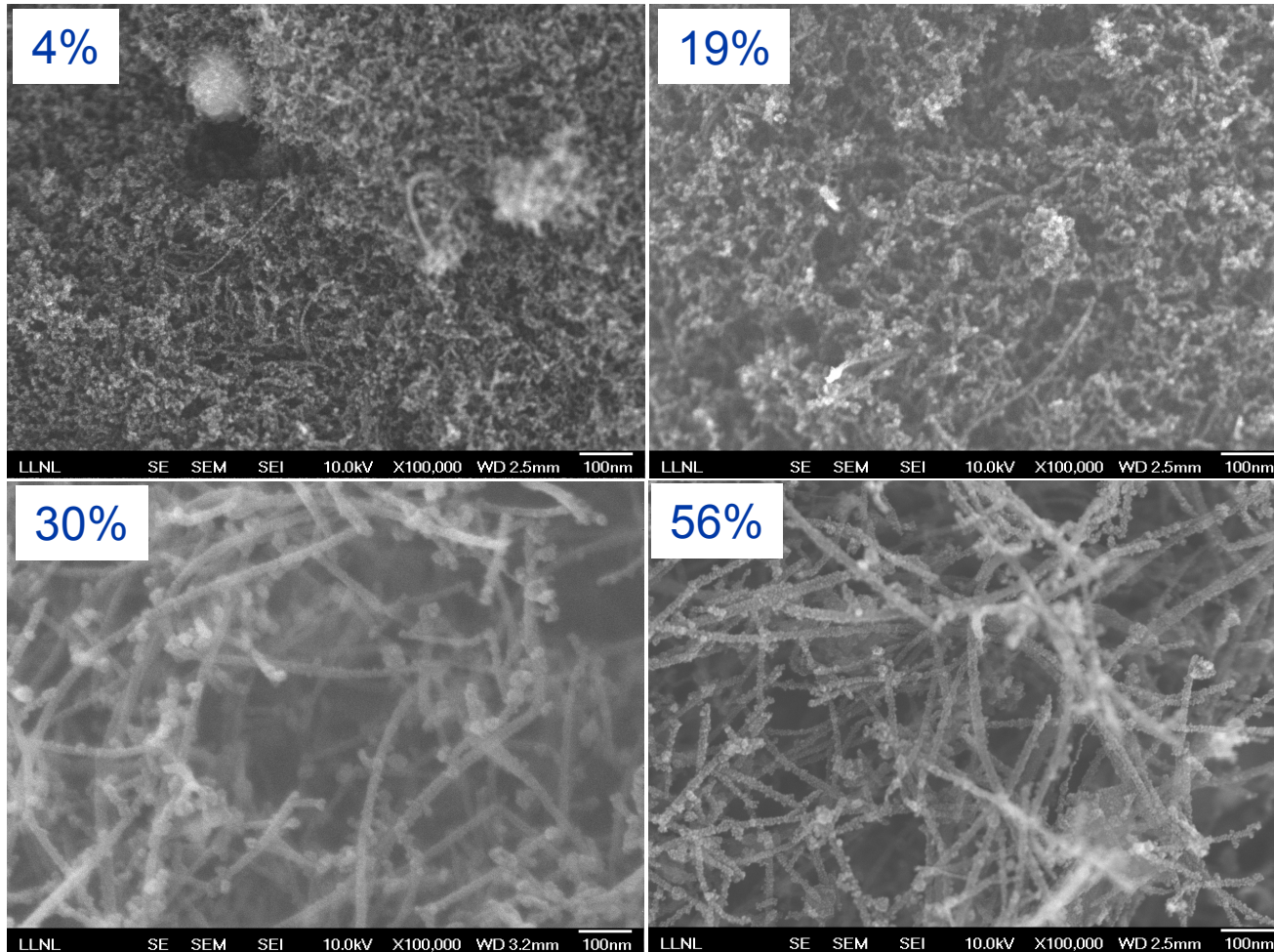
ACKNOWLEDGMENTS



BACKUP SLIDES

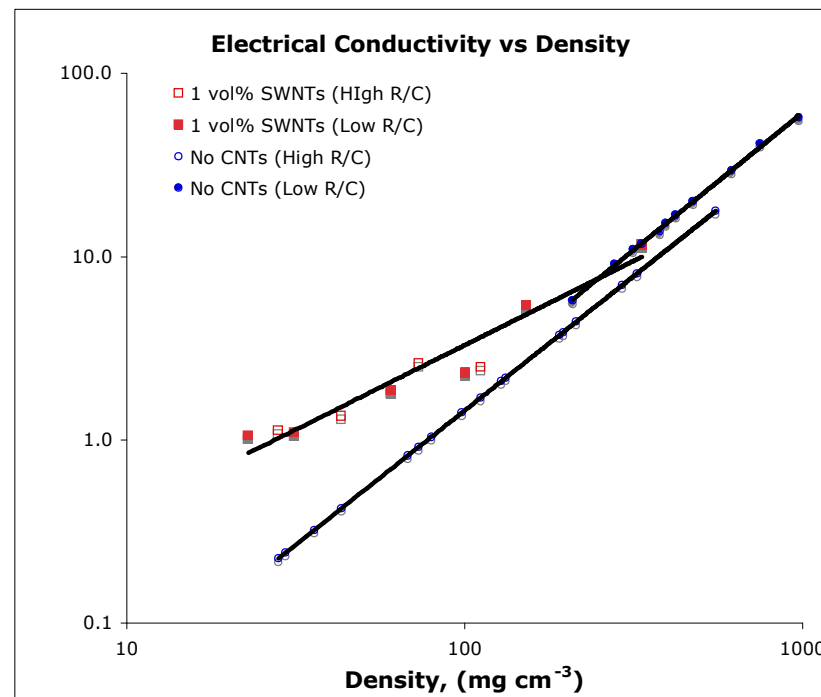
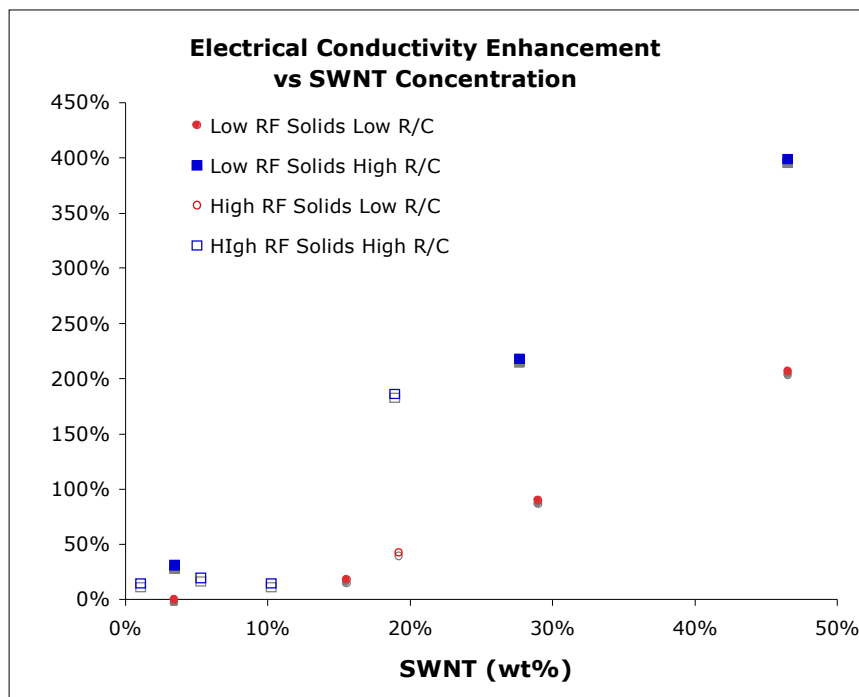


SWNT-CA: Foam morphology changes



Dramatic change in foam structure at high nanotube loadings (> 20 wt%)

SWNT-CA Composite: Electrical conductivity enhanced

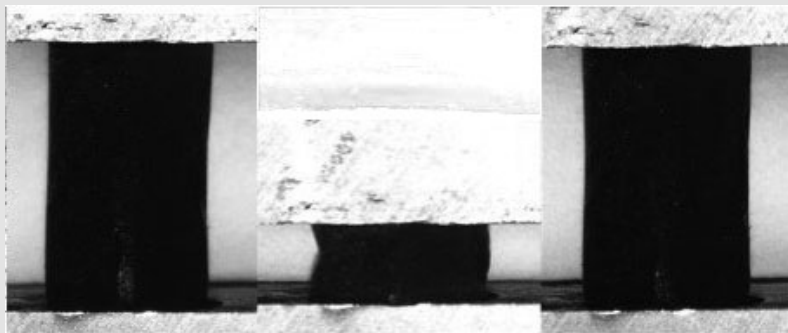


SWNTs improve electrical conductivity (~400% increase at 46 wt%)

Electrical conductivity of 1 vol% SWNT-CAs *do not* follow density scaling of pristine CAs ⇒ different foam morphology

SWNT-CA: Exhibit elastic behavior up to large strains

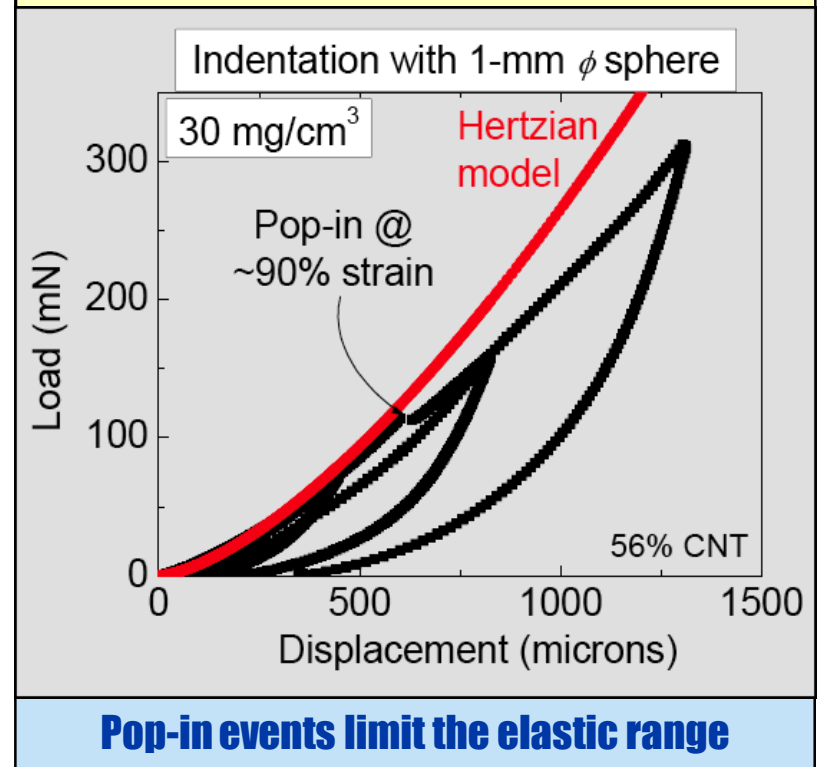
Large elastic range



Complete recovery after uniaxial compression to ~70% strain

- Low-density ($<50 \text{ mg/cm}^3$) foams exhibit large (70-90%) fracture strains
- Deformation depends on both density and nanotube loading
- Energy dissipation is similar to that observed for nanotube mats

Large elastic range



Stiff “sponges” with huge fracture strains instead of traditionally fragile aerogels

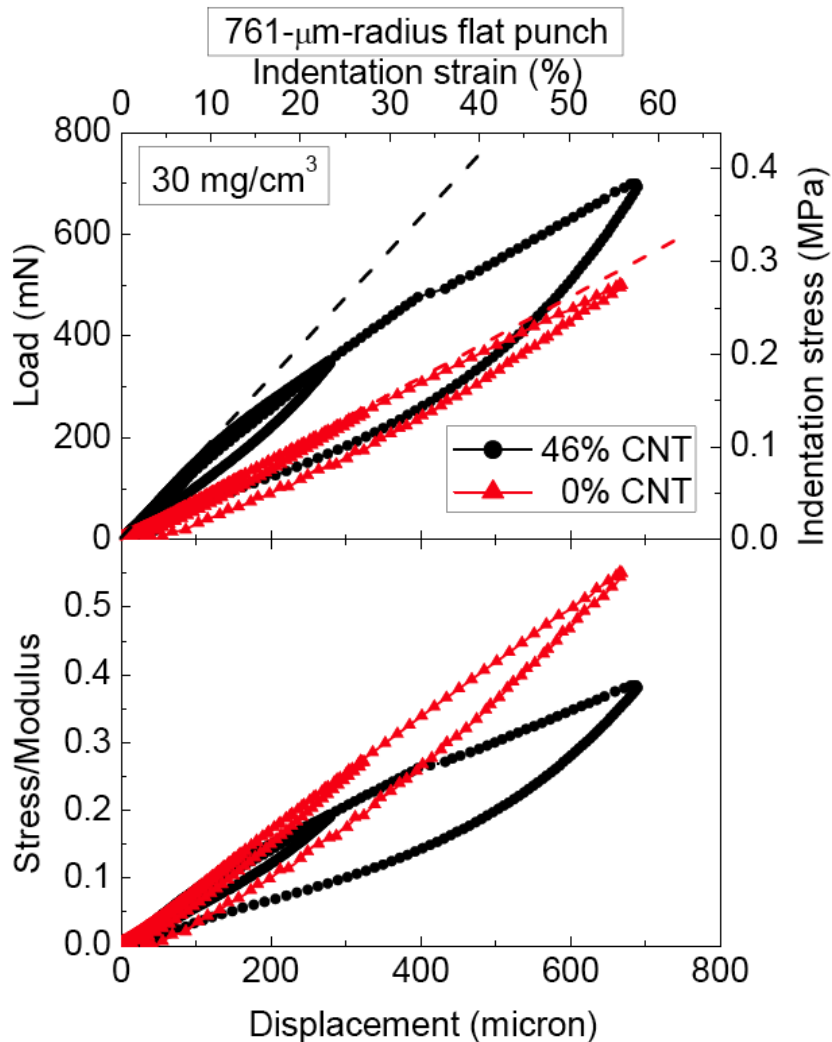
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Summary

- A novel class of nanoporous graphitic carbon foams has been synthesized
- Unprecedented properties: Electrically conductive, thermally stable ($>1000\text{ }^{\circ}\text{C}$), and mechanically robust
- Improved transport properties (DWNT-CA, SWNT-CA):
 - Greater than 100% enhancement in thermal conductivity
 - 100-400% improvement in electrical conductivity
- Rich mechanical deformation behavior (SWNT-CA):
 - Stiff ($\sim 100\%$ improvement of elastic modulus)
 - Energy dissipation
 - Fracture toughness
 - Fatigue behavior
- Implications for energy-related technologies
 - Hydrogen storage
 - Fusion and fission energy
 - Catalysis
 - Electrochemical energy storage
 - Composites with foam scaffolds



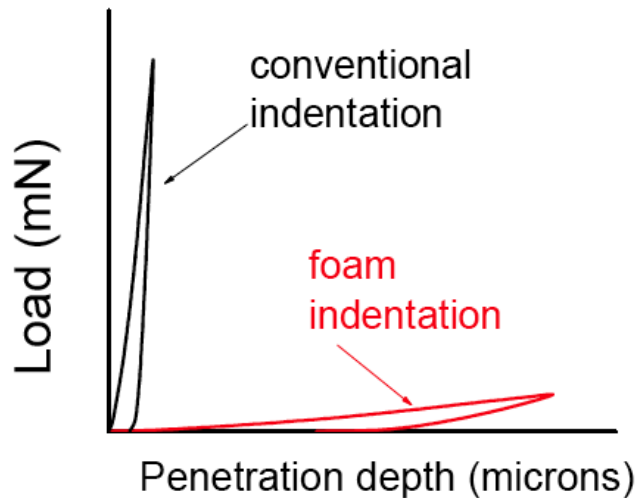
SWNT-CA: Exhibit nonlinear elastic behavior with energy dissipation



- Loading elastic modulus decreases with increasing strain
- Elastic nonlinearity is attributed to buckling of high-aspect-ratio nanoligaments
- Elastic nonlinearity increases for samples with larger nanotube loading
- Energy dissipation is attributed to
 - van der Waals interaction of ligaments
 - dissipative movement of air filling the pore volume

Loading with carbon nanotubes increases energy dissipation and nonlinear behavior

We use low-load, large-displacement indentation to study nanomechanics of foams



Spherical indentation :

$$P = \frac{4}{3} E^r \sqrt{R} h^{3/2}$$

$$E_{unload}^r = \frac{\sqrt{\pi} (dP / dh)^{unload}}{2\sqrt{A(h_{contact})}}$$

$$\text{Stress} = \frac{P}{A(h_{contact})} (\equiv \text{hardness})$$

$$\text{Strain} = \frac{4a}{3\pi R} \quad (a = \text{contact radius})$$

Flat punch indentation :

$$P = 2E^r R h$$

$$E_{unload}^r = \frac{(dP / dh)^{unload}}{2R}$$

$$\text{Stress} = \frac{P}{A} = \frac{P}{\pi R^2}$$

$$\text{Strain} = \frac{2}{\pi R} h$$

MTS XP Nanoindenter.

Oliver-Pharr analysis.

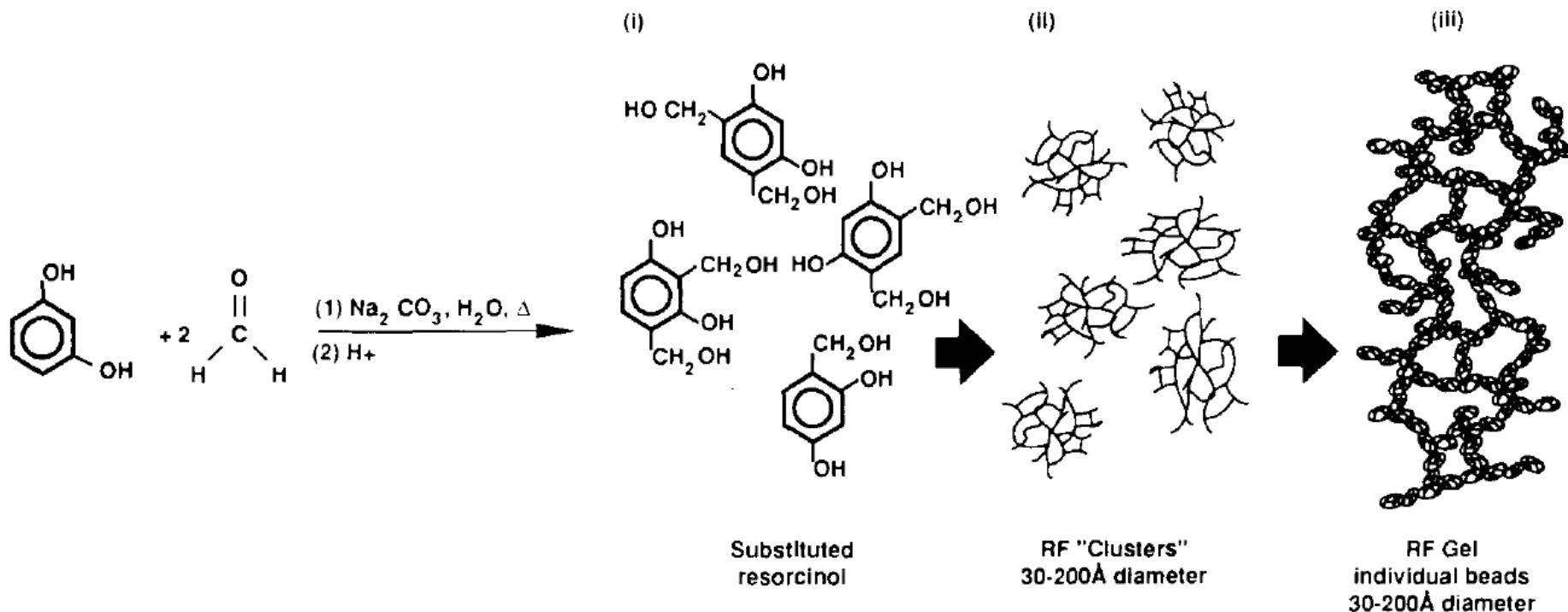
Major challenge of foam indentation = Low material stiffness

Contact stiffness < Instrument Stiffness (~10-100 N/m) \Rightarrow Incorrect surface determination \Rightarrow (Gross) overestimation of mechanical properties

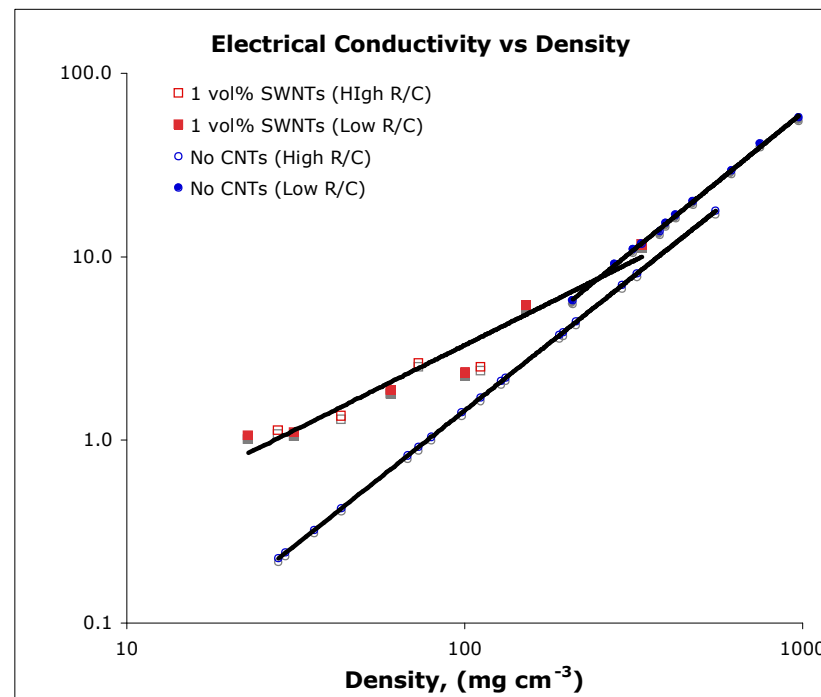
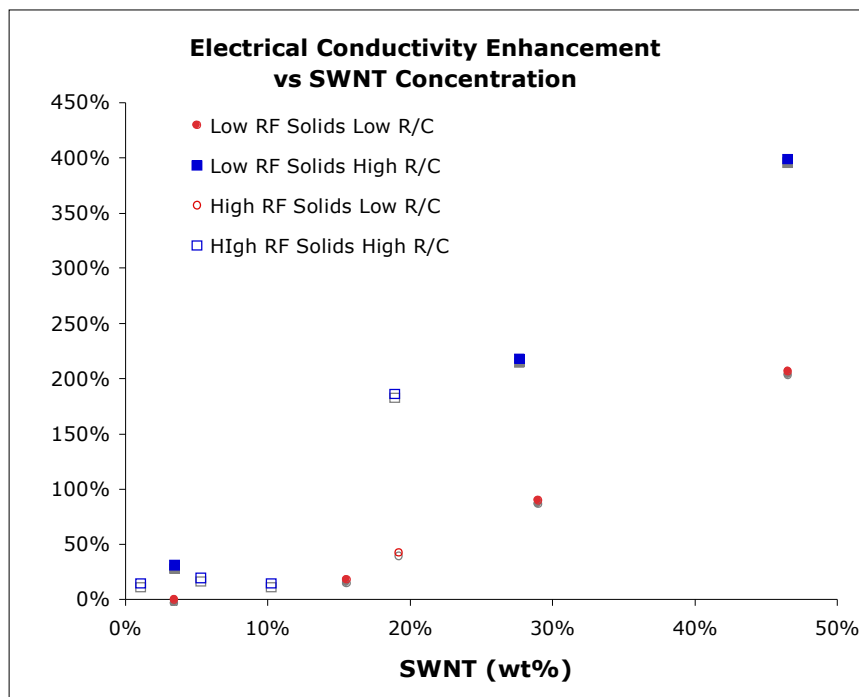
Penetration depths and contact areas are much larger than in conventional nanoindentation

Large *spherical* (R = 496, 986 microns) and *flat punch* (R = 31, 761 microns) tips were used to measure ultralow-density foams

RF Sol-Gel Chemistry



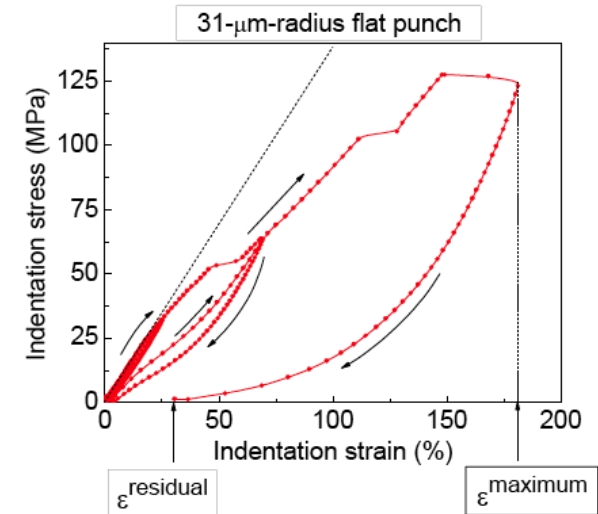
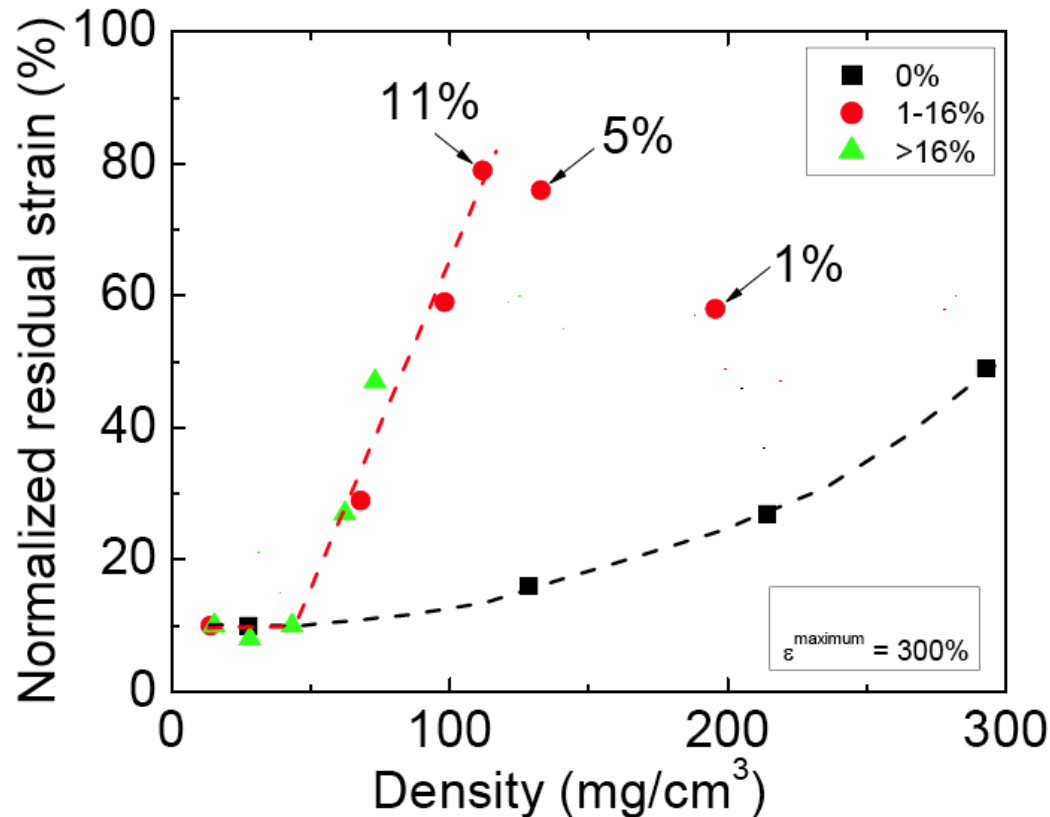
SWNT-CA Composite: Electrical conductivity enhanced



SWNTs improve electrical conductivity (~400% increase at 46 wt%)

Electrical conductivity of 1 vol% SWNT-CAs *do not* follow density scaling of pristine CAs ⇒ different foam morphology

Fracture behavior depends on both nanotube loading and monolith density



For densities $>50 \text{ mg/cm}^3$, nanotube-based foams have better elastic but inferior fracture properties than those of conventional carbon aerogels

Ultralow-density ($<50 \text{ mg/cm}^3$) foams have superior elastic and fracture properties

